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(54) Catalysts for hydrotreating hydrocarbons and method of activating the same.

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Description

This invention relates to a catalyst for hydrotreating hydrocarbon oil that can be easily activated, and to a method of activating the same.

5 For the so-called hydrotreatment process (treatment of hydrocarbon oil in the presence of hydrogen to effect hydrogenation, hydrodesulfurization, hydrodenitrification and hydrogenolysis), have been used those catalysts which comprise, as active ingredient, at least one member selected from the group consisting of the metals in the Periodic Table's Groups VI and VIII and are supported on an inorganic oxide carrier, such as alumina, silica-alumina and titania. Molybdenum and tungsten are frequently used as the Group VI metal,
10 and cobalt and nickel are often employed as the Group VIII metal.

These metals, usually supported on a carrier in the form of inactive oxide, must be activated before use by presulfiding for conversion from the oxide to sulfide form.

This presulfiding is generally effected by charging the catalyst to be activated in a reactor for hydrotreatment of hydrocarbon oil and passing a sulfurizing agent together with hydrogen gas through the
15 catalyst bed. The conditions of this presulfiding vary with the type of intended hydrotreatment process and the kind of sulfurizing agent used. When hydrogen sulfide is employed as the sulfurizing agent, it is diluted with hydrogen gas to a concentration of about 0.5 to 5 volume % and the resulting gaseous mixture is passed at a temperature higher than 180°C (usually higher than 250°C) in an amount of 1000 to 3000 litres (at standard temperature and pressure) for 1 litre of catalyst. When carbon disulfide, n-butylmercaptan,
20 dimethyl sulfide or dimethyl disulfide is used, it is diluted before use with light hydrocarbon oil and sulfurization is carried out at a temperature of 250 to 350°C, under a pressure of 20 to 100 Kg/cm², at a liquid space velocity of 0.5 to 2 hr⁻¹ and with a hydrogen/oil ration of 200 to 1000 Nl/l. After finishing this presulfiding of catalyst, feedstock to be treated is fed to the reactor to start the hydrotreatment process.

This presulfiding step, on which successful operation of the succeeding hydrotreatment process
25 depends, must be performed with great care by using proper materials. When a diluent is used, for example, a hydrocarbon oil containing no olefin must be selected, as otherwise the catalyst is poisoned by the polymeric substances formed from the olefins contained. In addition, heavy oil is unsuitable as the diluent because of its poor wetting on catalyst surface due to the high viscosity. As a result, light hydrocarbon oil has to be used as the diluent, leading to an increase in production cost. Furthermore, the
30 sulfurizing agent must be used in a relatively large amount to prevent the catalyst reduction from being inactivated by the reaction with hydrogen at high temperatures, and hence the weight ratio of sulfurizing agent to hydrogen must be maintained at a proper level throughout the presulfiding process. This preliminary step is rarely automated, and requires unusual and cumbersome operations, imposing a heavy burden on the operators. Thus, how to eliminate this presulfiding step, or how to minimize the cumbersome
35 operations involved, has been a subject of major concern.

A method to meet this demand was recently proposed, which comprises impregnating a supported catalyst of an active metal with a polysulfide represented by the general formula of R-S_n-R' (wherein n is an integer of 3 to 20, and R and R' are each hydrogen atom or an organic group of 1 to 150 carbon atoms), and heat-treating the polysulfide-impregnated catalyst in the absence of hydrogen gas at a temperature of
40 65 to 275°C and under a pressure of 0.5 to 70 bar [Japanese Patent Kokai No.111144 equivalent to EP-A-0181254 (1986)]. This method, in which the active metal is sulfurized by the polysulfide contained in the catalyst upon heating, eliminates the use of any sulfurizing agent and a diluent therefore when presulfiding is allowed to proceed inside the reactor, thus simplifying the operation. This method also makes it possible to effect presulfiding outside the reactor and to start hydrotreatment process immediately after the
45 sulfurized catalyst is charged in the reactor. However, the polysulfide has to be used in the form of a solution in an organic solvent for impregnation, and hence a special contrivance is needed for the use of organic solvents in carrying out the impregnation process.

SUMMARY OF THE INVENTION

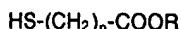
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The object of this invention is to eliminate the aforementioned problems associated with the conventional catalysts, and to provide a new catalyst for hydrotreating hydrocarbon oil that can be easily sulfurized for activation and a method of activating the same.

Comprehensive studies to seek for new sulfurizing agents easier to handle than the above-mentioned
55 polysulfides have led us to find that organic compounds having mercapto radical (-SH) are best suited for the purpose. This invention was accomplished based on these findings.

Thus, the first aspect of this invention relates to a catalyst for hydrotreating hydrocarbons, the catalyst being supported on an inorganic oxide carrier and comprising: (a) at least one oxide of a metal in Periodic

Table Groups VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) being a mercapto-carboxylic acid or acid derivative represented by the following general formula:



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wherein n is an integer of 1 to 3; and R denotes a hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group, or a linear, branched or saturated cyclic hydrocarbonaceous radical of 1 to 10 carbon atoms.

The second aspect of this invention relates to a method of activating the catalyst as defined above by treatment at a temperature from room temperature to 400 °C in the presence of hydrogen gas, said catalyst comprising (a) at least one oxide of a metal in Periodic Table Group VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH), being a mercapto-carboxylic acid represented by the following general formula:



wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or saturated cyclic hydrocarbonaceous radical of 1 to 10 carbon atoms.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

As is well known, alumina, silica-alumina, titania and others are used as the inorganic oxide carrier for catalysts of this type. Of these, alumina and silica-alumina are the most typical examples.

It is also known that molybdenum and/or tungsten are preferable as the active metal of Group VI, and cobalt and/or nickel are preferred examples of the active metal of Group VIII. The oxides of these metals may be used either alone or in combination.

The catalyst of this invention may also contain, as active component, oxide of phosphorus in addition to oxides of Group VI and Group VIII metals. Phosphorus may be deposited on the carrier either separately or simultaneously with the active metals. In the latter case in which a solution containing all the active components is used for impregnation, the largest possible amount of phosphorus that can be included in the catalyst is 8 weight % as P₂O₅ because the treating solution becomes more viscous as its phosphorus content increases, making impregnation increasingly less effective.

As preferable examples of the sulfurizing agents, there may be mentioned the following compounds: mercapto-carboxylic acids represented by the general formula, HS-(CH₂)_nCOOR (wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or saturated cyclic hydrocarbonaceous radical of 1 to 10 carbon atoms), such as mercaptoacetic acid (HSCH₂COOH), β-mercaptopropionic acid (HSCH₂CH₂COOH), alkali metal, alkaline earth metal salts thereof, methyl mercaptoacetate (HSCH₂COOCH₃), ethyl 2-mercaptopropionate (HSCH₂COOC₂H₅), ethylhexyl 2-mercaptopropionate (HSCH₂COOC₈H₁₇) and methyl 3-mercaptopropionate HSCH₂CH₂COOCH₃.

A solution of the above-mentioned sulfurizing agent (mercapto-carboxylic acid) is soaked by impregnation into an inorganic carrier bearing at least one member selected from the metals in the Periodic Table's Groups VI and VIII. In this case, use of an aqueous solution is most advantageous in terms of cost.

The preferable amount of sulfurizing agent (mercapto-carboxylic acid) to be included is 1 to 3 equivalent proportions based on the weight required for converting the Group VI and/or VIII metals to a sulfurized state highly active for hydrogenation (for example, MoS₂, WS₂, CoS and NiS). A smaller amount results in lower catalytic activity, while use of a larger amount is uneconomical because no marked enhancement of activity cannot be expected.

Some catalysts soaked with a solution of sulfurizing agent show activity without any further treatment; in other cases, however, activity can be exhibited by removing the solvent used for dissolving the sulfurizing agent, followed by treatment in the presence of hydrogen gas at a temperature in the range from room temperature to 400 °C (the solvent removal may be performed during the activation step in the presence of hydrogen gas).

During the activation step in the presence of hydrogen gas, the sulfurizing agent attached to the active metal through coordinate bond undergoes hydrogenolysis, converting the metal component into sulfided form which is an active species for hydrogenation. In effecting this activation process, there is no specific limitation upon the reaction pressure, and presence of hydrocarbons in the reaction system causes no problem. Hence, this step may be carried out in the reactor used for hydrocarbon hydrotreatment or in a

separate activation apparatus.

Activation is conducted at a temperature in the range from room temperature to 400 °C, preferably in the range from 100 to 300 °C. A treating temperature higher than 400 °C results in lowered catalytic activity.

The catalysts prepared by the method of this invention show higher activity in hydrodesulfurization of hydrocarbon oil than those sulfurized by the conventional method. The reason is not absolutely clear yet, but it may be assumed that the sulfurizing agent used herein (mercapto-carboxylic acids) is attached to the Group VI and/or VIII metal through coordinate bond and this is effective in forming the metal sulfides favorable in the succeeding activation step.

The following Examples and Comparative Examples will further illustrate the invention.

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Example 1

Twenty grams of a commercial catalyst containing 15 weight % of MoO₃ and 4 weight % of CoO supported on γ-alumina (KF-742; product of Nippon Ketjen Co., Ltd.) was thoroughly impregnated with 12 ml of an aqueous solution containing 6.0 g mercaptoacetic acid (d²⁰: 1.33) and dried at 80 °C for 16 hours, giving catalyst A₁. Catalysts A₂ and A₃ were prepared in much the same manner as above, except that 9.0 g and 12.0 g of mercaptoacetic acid were used, respectively. Catalyst A₄ was prepared by impregnating 20 g of the commercial catalyst (KF-742) with 12 ml of an aqueous solution containing 7.5 g mercaptoacetic acid, drying at 80 °C for 16 hours, and repeating the impregnation and drying steps once again.

20 The amounts of mercaptoacetic acid loaded on catalysts A₁, A₂, A₃ and A₄ were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

Separately, 500 g of an alumina carrier (specific surface area: 310 m²/g; pore volume: 0.70 ml/g) used in KF-742 was impregnated with a solution prepared from 111 g ammonium paramolybdate, 101 g nickel nitrate hexahydrate 150 g conc. ammonia water and water, dried at 110 °C for 16 hours and calcined at 500 °C for two hours, giving a catalyst containing 15 weight % of MoO₃ and 4 weight % of NiO. This base catalyst was then treated in the same manner as above to include varying amounts of mercaptoacetic acid, affording catalysts A₅, A₆, A₇ and A₈.

25 The amounts of mercaptoacetic acid loaded on catalysts A₅, A₆, A₇ and A₈ were respectively 1.2, 1.8, 2.4 and 3.0 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

30 In addition, 20 g of the commercial catalyst (KF-742) was thoroughly impregnated with 12 ml of an aqueous solution containing 10.0 g mercaptopropionic acid (d²⁰: 1.22) and dried at 80 °C for 16 hours, giving catalyst A₉.

35 The amount of mercaptopropionic acid included in this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

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(Activation)

40 Three millilitres each of the catalysts prepared above (A₁, A₂, A₃, A₄, A₅, A₆, A₇ and A₈) was charged in a fixed-bed flow reactor made of stainless steel and activated under the conditions shown below.

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Amounts of catalyst	3 ml
Pressure	Atmospheric pressure
Hydrogen flow rate	4.8 Nl/hr
Reaction time	3 hours
Reaction temperature	200 °C

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55 The catalysts thus activated were used for hydrodesulfurization of straight-run gas oil distilled from Kuwait crude oil: hereinafter abbreviated as KSRGO. For catalyst A₂, the substance not subjected to the activation process (referred to as catalyst A₂') was also tested in the same way as above. The properties of the KSRGO used for the reaction were:

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Specific gravity (15/4 °C)	0.848
Sulfur (% by weight)	1.61
Nitrogen (ppm by weight)	157
Initial boiling point (°C)	211
50 vol-% boiling point (°C)	340
Final boiling point (°C)	406

The reaction was conducted under the conditions shown below using a fixed-bed reactor.

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Amount of catalyst	3 ml
Liquid space velocity of feed oil	2.0 hr ⁻¹
Pressure (hydrogen pressure)	30 kg/cm ²
Reaction temperature	330 °C
Hydrogen/oil ratio	300 Nl/l
Reaction time	8 hours

Hydrotreated oil samples were taken from reactor at an interval of two hours for determination of sulfur content. The average desulfurization rate obtained from the oil analysis for 4 hours, 6 hours and 8 hours after the start of reaction is shown in Table 1.

Comparative Example 1

25 The catalysts of MoO₃/CoO and MoO₃/NiO types (hereinafter abbreviated as Mo/Co and Mo/Ni types) used in Example 1 and 2 were subjected to presulfiding using n-butylmercaptan diluted with KSRGO, and tested for hydrodesulfurization activity.

(Sulfurizing treatment)

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Sulfurizing agent	3 wt-% n-butylmercaptan in KSRGO
Amount of catalyst	3 ml
Liquid space velocity of feed oil	2.0 hr ⁻¹
Reaction pressure	30 Kg/cm ²
Reaction temperature	316 °C
Hydrogen/oil ratio	300 Nl/l
Reaction time	8 hours

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(Activity evaluation)

Catalytic activity was evaluated under the same conditions as in Example 1. The average desulfurization rate for 4 hours, samples taken 4 hours, 6 hours and 8 hours after the start of reaction is shown in Table 1.

45 For both of the Mo/Co and Mo/Ni types, catalysts containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than those sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO. With the catalysts of Mo/Co type, addition of mercaptoacetic acid in an amount of 1.2 times the theoretical weight required to convert the two metals into MoS₂ and CoS suffices, with no marked enhancement of activity being observed with a larger amount. Catalyst A₂ was slightly lower in activity than catalyst A₂, but showed higher activity than catalysts sulfurized with n-butylmercaptan by the conventional method. With the catalysts of Mo/Ni type, on the other hand, the optimum amount of mercaptoacetic acid to be added was somewhat larger than with catalysts of Mo/Co type, but did not exceed a level of 1.8 times the theoretical weight.

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R sults of Activity Evaluation Using KSRGO

Table 1-(1) (Mo/Co type)

Catalyst	A ₁	A ₂	A' ₂	A ₃	A ₄	Sulfurized with n-BM(*)
Content of mercapto-acetic acid(**)	x1.2	x1.8	x1.8	x2.4	x3.0	—
Rate of desulfurization (%)	88.2	87.5	86.7	87.3	87.3	82.7

Table 1-(2) (Mo/Ni type)

Catalyst	A ₅	A ₆	A ₇	A ₈	Sulfurized with n-BM(*)
Content of mercapto-acetic acid(**)	x1.2	x1.8	x2.4	x3.0	—
Rate of desulfurization (%)	81.2	84.2	83.9	83.7	79.1

Table 1-(3) (Mo/Co type)

Catalyst	A ₉	Sulfurized with n-BM(*)
Content of mercaptopropionic acid (**)	x1.3	—
Rate of desulfurization (%)	87.5	82.7

(*) Sulfurized with 3 wt % n-butylmercaptan in KSRGO.

(**) Factor based on the theoretical weight required for conversion into MoS₂, CoS and NiS.

[The same applies to the subsequent tables for (*) and (**).]

Example 2

One hundred grams of γ -alumina carrier (specific surface area: 280 m²/g; pore volume: 0.75 ml/g) was impregnated with 80 ml of an aqueous solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 16.5 g of 85% phosphoric acid and water, dried at 110 °C for 16 hours and calcined at 500 °C for two hours, giving a catalyst containing 20 weight % of MoO₃, 4 weight % of NiO and 7 weight % of P₂O₅. This base catalyst (20 g) was thoroughly impregnated with 10 ml of an aqueous solution containing 7.3 g mercaptoacetic acid and dried at 100 °C for 16 hours, affording catalyst B₁.

Catalysts B₂ and B₃ were prepared in much the same manner as above, except that 11.0 g and 14.6 g of 100% mercaptoacetic acid were used, respectively, in place of the aqueous solution.

The amounts of mercaptoacetic acid loaded on catalysts B₁, B₂ and B₃ were respectively 1.0, 1.5 and 2.0 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Separately, 20 g of the calcined catalyst prepared above was thoroughly impregnated with an aqueous solution containing 11.7 g mercaptopropionic acid and dried at 100 °C for 16 hours, giving catalyst B₄. The amount of mercaptopropionic acid loaded on this catalyst was 1.5 times the theoretical amount required to

convert the two metals into MoS₂ and NiS.

(Activity evaluation)

5 Catalysts B₁, B₂, B₃ and B₄ were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 1. The average desulfurization rates are shown in Table 2.

Comparative Example 2

10 The base catalyst of MoO₃/NiO/P₂O₅ type (hereinafter abbreviated as Mo/Ni/P type) used in Example 2 was sulfurized in the same manner as in Comparative Example 2, and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average desulfurization rate is also shown in Table 2.

15 **Table 2 Results of Activity Evaluation Using KSRGO**

Catalyst	B ₁	B ₂	B ₃	B ₄	Sulfurized with n-BM(*)
Content of sulfurizing agent(**)		HSCH ₂ COOH		HSCH ₂ CH ₂ COOH	—
	x1.0	x1.5	x2.0	x1.5	
Rate of desulfurization (%)	89.6	93.5	93.0	93.4	73.5

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The catalysts containing mercaptoacetic acid or mercaptopropionic acid showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO. Data of the catalysts containing mercaptoacetic acid indicate that addition of the acid in an amount of 1.5 times the theoretical weight required to convert the two metals into MoS₂, NiS and CoS suffices, with no marked enhancement of activity being observed with larger amounts. Excessively large amounts of sulfurizing agent included in a catalyst not only results in its waste, but also requires two or more steps for impregnation.

Example 3

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Twenty grams of commercial catalyst (the same type as used in Example 1) was thoroughly impregnated with 10.4 g of 100% methyl mercaptoacetate and dried at 80°C for 16 hours, giving catalyst C₁. Catalyst C₂ was prepared in much the same manner as above, except that 11.7 g of ethyl mercaptoacetate was used as sulfurizing agent. Catalyst C₃ was prepared by impregnating 20 g of the above commercial catalyst with 20.0 g of 2-ethylhexyl mercaptoacetate, drying at 80°C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of mercaptoacetate loaded on catalysts C₁, C₂ and C₃ were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

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Separately, the same commercial catalysts as above was thoroughly impregnated with 11.7 g of methyl 3-mercaptopropionate and dried at 80°C for 16 hours, giving catalyst C₄. The amount of methyl 3-mercaptopropionate loaded on this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS₂ and CoS.

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In addition, 500 g of alumina carrier (the same type as used in Example 1 for the preparation of catalysts A₅ through A₈) was impregnated with a solution prepared from 111 g ammonium paramolybdate, 101 g nickel nitrate hexahydrate and 150 g conc. ammonia water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 15 weight % of MoO₃ and 4 weight % of NiO. This base catalyst was then activated in the same manner as in Example 1 to include 10.4 g methyl mercaptoacetate, 11.7 g ethyl mercaptoacetate or 20.0 g 2-ethylhexyl mercaptoacetate, affording catalysts C₅, C₆ and C₇, respectively.

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The amounts of mercaptoacetate loaded on these catalysts were 1.8 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Furthermore, 20 g of the above base catalyst was thoroughly impregnated with 11.7 g methyl 3-mercaptopropionate and dried at 80°C for 16 hours, giving catalyst C₈.

The amount of m-thyl 3-mercaptopropionate loaded on this catalyst was 1.8 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts C₁, C₂, C₃, C₄, C₅, C₆, C₇ and C₈ prepared above were activated in the same manner as in Example 1 and used for hydrodesulfurization of KSRGO under the same conditions. The average desulfurization rates are shown in Table 3.

Comparative Example 3

The catalysts of Mo/Co and Mo/Ni types used in Example 3 were sulfurized in the same manner as in Comparative Example 1, and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average desulfurization rates are also shown in Table 3.

For both of the Mo/Co and Mo/Ni types, catalysts containing a mercaptoacetate or mercaptopropionate showed nearly the same activity as those sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

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Example 4

One hundred grams of γ -alumina carrier (the same type as used in Example 2) was impregnated with 80 ml of a solution prepared from 29.0 g molybdenum trioxide, 10.5 g nickel carbonate (Ni content: 43.3%), 20 16.5 g 85% of phosphoric acid and water, dried at 110°C for 16 hours and calcined at 500°C for two hours, giving a catalyst containing 20 weight % MoO₃, 4 weight % NiO and 7 weight % P₂O₅. This base catalyst (30 g) was then impregnated with

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Table 3-(1) (Mo/Co type)

Catalyst	C ₁	C ₂	C ₃	C ₄	Sulfurized with n-Bu(*)
Mercapto- carboxylate	Methyl merc- captoacetate	Ethyl merc- captoacetate	2-Ethylhexyl mercaptoacetate	Methyl 3-mer- captoacetate	—
Amount (**)	x1.8	x1.8	x1.8	x1.8	—
Rate of desul- furization (%)	82.2	82.7	83.3	83.7	82.7

Table 3-(2) (Mo/Ni type)

Catalyst	C ₅	C ₆	C ₇	C ₈	Sulfurized with n-Bu(*)
Mercapto- carboxylate	Methyl merc- captoacetate	Ethyl merc- captoacetate	2-Ethylhexyl mercaptoacetate	Methyl 3-mer- captoacetate	—
Amount (**)	x1.8	x1.8	x1.8	x1.8	—
Rate of desul- furization (%)	78.9	80.8	79.7	79.3	79.1

Table 4 (Mo/Ni/P type)

Catalyst	D ₁	D ₂	D ₃	D ₄	Sulfurized with n-Bu(*)
Mercapto- carboxylate	Methyl merc- captoacetate	Ethyl merc- captoacetate	2-Ethylhexyl mercaptoacetate	Methyl 3-mer- captoacetate	—
Amount (**)	x1.5	x1.5	x1.5	x1.5	—
Rate of desul- furization (%)	80.3	78.9	80.8	76.7	73.5

15.8 g methyl mercaptoacetate and dried at 100°C for 16 hours, affording catalyst D₁. Catalyst D₂ was prepared in much the same manner as above, except that 17.9 g of ethyl mercaptoacetate was used instead of methyl mercaptoacetate. Catalyst D₃ was prepared by impregnating the base catalyst (30 g) with 35.8 g 2-ethylhexyl mercaptoacetate, drying at 100°C for 16 hours, and repeating the impregnation and drying steps once again.

The amounts of mercaptoacetate loaded on catalysts D₁, D₂ and D₃ were 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

In addition, catalyst D₄ was prepared by impregnating the above base catalyst (30 g) with 21.0 g methyl 3-mercaptopropionate and drying at 100°C for 16 hours. The amount of methyl 3-mercaptopropionate loaded on this catalyst was 1.5 times the theoretical amount required to convert the two metals into MoS₂ and NiS.

Catalysts D₁, D₂, D₃ and D₄ prepared above were used for hydrodesulfurization of KSRGO without being activated under the same conditions as in Example 2. The average rates of desulfurization are shown in Table 4.

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Comparative Example 4

The base catalyst of Mo/Ni/P type used in Example 4 was sulfurized in the same manner as in Comparative Example 2 and used for hydrodesulfurization of KSRGO in the same way as in Example 1. The average rate of desulfurization is also shown in Table 4.

The catalysts of Mo/Ni/P type containing a mercaptoacetate or mercaptopropionate showed higher activity than the catalyst sulfurized with a mixture of 3 weight % n-butylmercaptan and KSRGO.

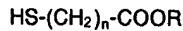
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Claims

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1. A catalyst for hydrotreating hydrocarbons the catalyst being supported on an inorganic oxide carrier and comprising: (a) at least one oxide of a metal in Periodic Table Groups VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH) being a mercapto-carboxylic acid or acid derivative represented by the following general formula:

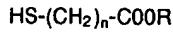
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wherein n is an integer of 1 to 3; and R denotes a hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group, or a linear, branched or saturated cyclic hydrocarbonaceous radical of 1 to 10 carbon atoms.

2. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said inorganic oxide carrier comprises at least one of alumina, silica-alumina and titania.
- 35 3. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said Group VI metal is molybdenum and/or tungsten and said Group VIII metal is cobalt and/or nickel.
4. A catalyst for hydrotreating hydrocarbons according to claim 3, wherein the catalyst also contains phosphorus as a component element.
- 40 5. A catalyst for hydrotreating hydrocarbons according to claim 1, wherein said mercapto-carboxylic acid is at least one of mercaptoacetic acid (HSCH₂COOH), β-mercaptopropionic acid (HSCH₂CH₂COOH), an alkali metal, an alkaline earth metal and ammonium salts thereof, methyl 2-mercaptopacetate (HSCH₂COOCH₃), ethyl mercaptoacetate (HSCH₂COOC₂H₅), ethylhexyl mercaptoacetate (HSCH₂COOC₈H₁₇) and methyl 3-mercaptopropionate (HSCH₂CH₂COOCH₃).
- 50 6. A method of activating a hydrotreating catalyst for hydrocarbons according to any preceding claim by treatment at a temperature from room temperature to 400°C in the presence of hydrogen gas, said catalyst comprising (a) at least one oxide of a metal in Periodic Table Group VI or VIII, and (b) at least one organic compound having a mercapto radical or radicals (-SH), being a mercapto-carboxylic acid or acid derivative represented by the following general formula:

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wherein n is an integer of 1 to 3; and R denotes hydrogen atom, an alkali metal, an alkaline earth metal, ammonium group, or a linear, branched or saturated cyclic hydrocarbonaceous radical of 1 to 10 carbon atoms.

7. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 6, in which said inorganic oxide carrier comprises at least one of alumina, silica-alumina and titania.

8. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 6, wherein said Group VI metal is molybdenum and/or tungsten and said Group VIII metal is cobalt and/or nickel.

9. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 8, wherein said catalyst also contains phosphorus as a component element.

10. A method of activating a hydrotreating catalyst for hydrocarbons according to claim 6, wherein said mercaptocarboxylic acid is at least one of mercaptoacetic acid ($\text{HSCH}_2\text{C}(\text{O})\text{H}$), β -mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{C}(\text{O})\text{H}$), an alkali metal, an alkaline earth metal, methyl 2-mercptoacetate ($\text{HSCH}_2\text{C}(\text{OOC})\text{CH}_3$), ethyl 2-mercptoacetate ($\text{HSCH}_2\text{C}(\text{OOC}_2)\text{H}_5$), 2-ethylhexyl mercaptoacetate ($\text{HSCH}_2\text{C}(\text{OOC}_8\text{H}_{17})$) and methyl 3-mercaptopropionate ($\text{HSCH}_2\text{CH}_2\text{C}(\text{OOC})\text{CH}_3$).

15. 11. A method of activating hydrotreating catalysts for hydrocarbons according to claim 6, wherein said temperature is in the range from 100 to 300 °C.

Patentansprüche

20. 1. Katalysator für das Hydrotreating von Kohlenwasserstoffen, wobei der Katalysator auf einem anorganischen oxidischen Träger gehalten ist und umfaßt: (a) zumindest ein Oxid eines Metalls aus der Gruppe VI oder VIII der Tabelle des Periodensystems und (b) zumindest eine organische Verbindung mit einem Mercapto-Radikal oder Radikalen (-SH) in Form einer Mercapto-Carbonsäure oder eines Säurederivats, dargestellt durch die folgende allgemeine Formel:

$$\text{HS-(CH}_2)_n\text{-COOR}$$

30. wobei n eine ganze Zahl von 1 bis 3 ist; und R bezeichnet ein Wasserstoffatom, Alkalimetall, Erdalkalimetall, eine Ammoniumgruppe oder ein lineares, verzweigtes oder gesättigtes cyklisches kohlenwasserstoffsitziges Radikal mit 1 bis 10 Kohlenstoffatomen.

35. 2. Katalysator für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 1, wobei der genannte anorganische oxidische Träger zumindest einen aus Aluminiumoxid, Siliciumdioxid-Aluminiumoxid und Titandioxid umfaßt.

40. 3. Katalysator für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 1, wobei das genannte Metall der Gruppe VI Molybdän und/oder Wolfram ist und das genannte Metall der Gruppe VIII Kobalt und/oder Nickel.

45. 4. Katalysator für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 3, wobei der Katalysator auch Phosphor als eine Elementkomponente enthält.

50. 5. Katalysator für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 1, wobei die genannte Mercapto-Carbonsäure zumindest eine aus Mercaptoessigsäure (HSCH_2COOH), β -Mercaptopropionsäure ($\text{HSCH}_2\text{CH}_2\text{COOH}$), Alkalimetall-, Erdalkalimetall- und Ammoniumsalzen derselben, Methyl 2-Mercaptoacetat ($\text{HSCH}_2\text{COOCH}_3$), Ethylmercaptoacetat ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), Ethylhexylmercaptoacetat ($\text{HSCH}_2\text{COOC}_8\text{H}_{17}$) und Methyl 3-Mercaptopropionat ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$) ist.

55. 6. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach einem der vorhergehenden Ansprüche durch Behandlung bei einer Temperatur zwischen Raumtemperatur und 400 °C in Gegenwart von Wasserstoffgas, wobei der genannte Katalysator umfaßt (a) zumindest ein Oxid eines Metalls aus der Gruppe VI oder VIII der Tabelle des Periodensystems und (b) zumindest eine organische Verbindung mit einem Mercapto-Radikal oder Radikalen (-SH) in Form einer Mercapto-Carbonsäure oder eines Säurederivats, dargestellt durch die folgende allgemeine Formel:

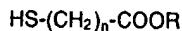
$$\text{HS-(CH}_2)_n\text{-COOR}$$

wobei n eine ganz Zahl von 1 bis 3 ist; und R bezeichnet ein Wasserstoffatom, Alkalimetall, Erdalkalimetall, eine Ammoniumgruppe oder ein lineares, verzweigtes oder gesättigtes cyklisches kohlenwasserstoffhaltiges Radikal mit 1 bis 10 Kohlenstoffatomen.

- 5 7. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 6, bei dem der genannte anorganische oxidische Träger zumindest einen aus Aluminiumoxid, Siliciumdioxid-Aluminiumoxid und Titandioxid umfaßt.
- 10 8. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 6, wobei das genannte Metall der Gruppe VI Molybdän und/oder Wolfram ist und das genannte Metall der Gruppe VIII Kobalt und/oder Nickel.
- 15 9. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 8, wobei der genannte Katalysator auch Phosphor als eine Elementkomponente enthält.
- 20 10. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 6, wobei die genannte Mercapto-Carbonsäure zumindest eine aus Mercaptoessigsäure (HSCH_2COOH), β -Mercaptopropionsäure ($\text{HSCH}_2\text{CH}_2\text{COOH}$), ein Alkalimetall, ein Erdalkalimetall, Methyl 2-Mercaptoacetat ($\text{HSCH}_2\text{COOCH}_3$), Ethyl 2-Mercaptoacetat ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), 2-Ethylhexylmercaptoacetat($\text{HSCH}_2\text{COOC}_8\text{H}_{17}$) und Methyl 3-Mercaptopropionat ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$) ist.
- 25 11. Verfahren zur Aktivierung eines Katalysators für das Hydrotreating von Kohlenwasserstoffen nach Anspruch 6, wobei die genannte Temperatur in einem Bereich von 100 bis 300 °C liegt.

25 Revendications

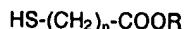
- 1. Catalyseur pour l'hydrotraitement d'hydrocarbures, le catalyseur étant supporté sur un support d'oxyde organique et comprenant : (a) au moins un oxyde d'un métal des groupes VI ou VIII du tableau périodique, et (b) au moins un composé organique ayant un ou des radicaux mercapto (-SH) qui est un acide mercaptocarboxylique ou un dérivé d'acide représenté par la formule générale suivante :



dans laquelle n est un entier de 1 à 3; et R est un atome d'hydrogène, de métal alcalin, de métal alcalino-terreux, un groupe ammonium ou un radical hydrocarboné linéaire, ramifié ou cyclique saturé de 1 à 10 atomes de carbone.

- 35 2. Catalyseur pour l'hydrotraitement d'hydrocarbures suivant la revendication 1, dans lequel ce support d'oxyde inorganique comprend au moins un support parmi l'alumine, la silice-alumine et l'oxyde de titane.
- 40 3. Catalyseur pour l'hydrotraitement d'hydrocarbures suivant la revendication 1, dans lequel ce métal du groupe VI est le molybdène et/ou le tungstène, et ce métal du groupe VIII est le cobalt et/ou le nickel.
- 45 4. Catalyseur pour l'hydrotraitement d'hydrocarbures suivant la revendication 3, dans lequel le catalyseur contient aussi du phosphore en tant qu'élément composant.
- 50 5. Catalyseur pour l'hydrotraitement d'hydrocarbures suivant la revendication 1, dans lequel cet acide mercaptocarboxylique est au moins un composé parmi l'acide mercaptoacétique (HSCH_2COOH), l'acide β -mercaptopropionique ($\text{HSCH}_2\text{CH}_2\text{COOH}$), un sel de métal alcalin, de métal alcalino-terreux et d'ammonium de ceux-ci, le 2-mercptoacétate de méthyle ($\text{HSCH}_2\text{COOCH}_3$), le 2-mercptoacétate d'éthyle ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), le 2-mercptoacétate d'éthylhexyle ($\text{HSCH}_2\text{COOC}_8\text{H}_{17}$) et le 3-mercaptopropionate de méthyle ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$).
- 55 6. Procédé pour activer un catalyseur d'hydrotraitement pour hydrocarbures suivant l'une quelconque des revendications précédentes par traitement à une température allant de la température ambiante à 400 °C en présence d'hydrogène gazeux, ce catalyseur comprenant : (a) au moins un oxyde d'un métal des groupes VI ou VIII du tableau périodique, et (b) au moins un composé organique ayant un ou des

radicaux mercapto (-SH) qui est un acide mercapto-carboxylique ou un dérivé d'acide représenté par la formule générale suivant :



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dans laquelle n est un entier de 1 à 3; et R est un atome d'hydrogène, de métal alcalin, de métal alcalino-terreux, un groupe ammonium ou un radical hydrocarboné linéaire, ramifié ou cyclique saturé de 1 à 10 atomes de carbone.

- 10 7. Procédé pour activer un catalyseur d'hydrotraitements pour hydrocarbures suivant la revendication 6, dans lequel ce support d'oxyde inorganique comprend au moins un support parmi l'alumine, la silice-alumine et l'oxyde de titane.
- 15 8. Procédé pour activer un catalyseur d'hydrotraitements pour hydrocarbures suivant la revendication 6, dans lequel ce métal du groupe VI est le molybdène et/ou le tungstène, et ce métal du groupe VIII est le cobalt et/ou le nickel.
- 9. Procédé pour activer un catalyseur d'hydrotraitements pour hydrocarbures suivant la revendication 8, dans lequel le catalyseur contient aussi du phosphore en tant qu'élément composant.
- 20 10. Procédé pour activer un catalyseur d'hydrotraitements pour hydrocarbures suivant la revendication 6, dans lequel cet acide mercaptocarboxylique est au moins un composé parmi l'acide mercaptoacétique (HSCH_2COOH), l'acide β -mercaptopropionique ($\text{HSCH}_2\text{CH}_2\text{COOH}$), un sel de métal alcalin, de métal alcalino-terreux et d'ammonium de ceux-ci, le 2-mercptoacétate de méthyle ($\text{HSCH}_2\text{COOCH}_3$), le 2-mercptoacétate d'éthyle ($\text{HSCH}_2\text{COOC}_2\text{H}_5$), le 2-mercptoacétate d'éthylhexyle ($\text{HSCH}_2\text{COOC}_8\text{H}_{17}$) et le 3-mercaptopropionate de méthyle ($\text{HSCH}_2\text{CH}_2\text{COOCH}_3$).
- 11. Procédé pour activer des catalyseurs d'hydrotraitements pour hydrocarbures suivant la revendication 6, dans lequel cette température est de l'ordre de 100 à 300 °C.

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